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An NMR spectroscopic study of the reactions of (2-(2-methoxyethoxy)ethyl)diphenylphosphine with rhodium(I) olefin complexes

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Abstract

The reactions of $Ph_2P(CH_2CH_2O)_2CH_3$ (I) with $[(cod)Rh(\mu\text{-}Cl)]_2$ and $[(coe)_2Rh(\mu\text{-}Cl)]_2$ (cod = 1,5-cyclooctadiene, coe = *cis*-cyclooctene) and of Ph_2PMe with $[(coe)_2Rh(\mu\text{-}Cl)]_2$ have been studied using ^{31}P and ^{13}C NMR spectroscopy. These studies indicate that the two Rh complexes give quite different reaction products. The reaction of I with $[(cod)Rh(\mu\text{-}Cl)]_2$ at a Rh/I ratio of 1/1 yields $(cod)Rh\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P\}Cl$ (II). Increasing the Rh/I ratio in this solution to 1/2 results in the formation of $ClRh\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P\}_3$ (III), but not of any complexes with two I's coordinated to Rh. A complex with two I's attached to the Rh can be formed by first reacting II with $AgBF_4$ to form $[(cod)Rh\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P,O\}]BF_4$ (IV) and then by reacting IV with a second equivalent of I to form $[(cod)Rh\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P\}_2]BF_4$ (V). The reaction of $[(coe)_2Rh(\mu\text{-}Cl)]_2$ with Ph_2PMe yields $[(coe)(Ph_2PMe)Rh(\mu\text{-}Cl)]_2$ (VI) at a Rh/Ph_2PMe ratio of 1/1, $[(Ph_2PMe)_2Rh(\mu\text{-}Cl)]_2$ (VII) at a Rh/Ph_2PMe ratio of 1/2 and $ClRh(Ph_2PMe)_3$ (VIII) at a Rh/Ph_2PMe ratio of 1/3. The reaction of $[(coe)_2Rh(\mu\text{-}Cl)]_2$ with I gives a different product, $[\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P,O\}Rh(\mu\text{-}Cl)]_2$ (IX) at a Rh/I ratio of 1/1, but similar products at Rh/I ratios of 1/2, $[\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P\}_2Rh(\mu\text{-}Cl)]_2$ (XI) and 1/3, III. The differences in the reaction products are due to the fact that the bidentate cod ligand coordinates much more strongly to the Rh than do either the bridging chlorine or the monodentate coe ligand. Thus, the reactions of $[(cod)Rh(\mu\text{-}Cl)]_2$ with phosphines initially involve displacement of the bridging chloride, but those of $[(coe)_2Rh(\mu\text{-}Cl)]_2$ with phosphines initially involve loss of the coe ligand. The weak Rh–coe bond allows I to function as a chelating P/O-ligand in IX.

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Introduction

In recent years, the coordination chemistry of hemilabile ligands, particularly those containing both P and O donor sites, with Pt group metals has been extensively studied [1–10]. One reason for this is that the weakly coordinating hard donor atoms of the ligands can be easily displaced from the transition metals in solution to provide an open coordination site. This allows these complexes to serve as catalysts for reactions involving the coordination and activation of a variety of small molecules [6,10,11]. A second reason for interest in these ligands is that they may be able to form binuclear complexes containing both hard and soft metal centers [12]. These binuclear complexes are also of interest as catalysts for the activation of small bifunctional molecules such as carbon dioxide.

It is often difficult to isolate and analytically characterize complexes with these hemilabile ligands due to the lability of the hard donor atom. However, when the ligands also contain a P donor atom, the ^{31}P NMR spectra of the complexes often provide sufficient information to allow the coordination geometries of the complexes to be determined [13]. This is particularly true when one bond P–transition metal coupling constants can be observed.

We have previously reported the preparation and multinuclear NMR characterization of a variety of Pt-group metal complexes with the potentially tridentate (2-(2-methoxyethoxy)ethyl)diphenylphosphine ligand, I [14]. In all of these complexes, the ligands were observed to be coordinated in a monodentate fashion through the P. However, the only Rh complex that was isolated was quite unstable in solution, and this suggested that the coordination chemistry of Rh complexes might be of interest. Accordingly, we have carried out an NMR spectroscopic study of the reactions of I with $[(cod)Rh(\mu\text{-}Cl)]_2$ and $[(coe)_2Rh(\mu\text{-}Cl)]_2$ (cod = 1,5-cyclooctadiene, coe = *cis*-cyclooctene), and a parallel study of the reactions of Ph_2PMe with $[(coe)_2Rh(\mu\text{-}Cl)]_2$. The results of these studies are reported in this paper, and effects of the natures of the olefins and phosphine ligands on these natures reactions are discussed.

Experimental

Chemicals

The acetone-d_6 was purchased from Aldrich Chemical Co. It was received in ampules, and these were opened and handled in an inert atmosphere glove box equipped with a dry train. The methyldiphenylphosphine was purchased from Pressure Chemical Co. and was opened under nitrogen and used as received. Literature methods were used to prepare (2-(2-methoxyethoxy)ethyl)diphenylphosphine (I) [14], $[(1,5\text{-cyclooctadiene})Rh(\mu\text{-}Cl)]_2$ [15] and $[(cis\text{-cyclooctene})_2Rh(\mu\text{-}Cl)]_2$ [16].

NMR spectroscopy

The ^{31}P NMR and ^{13}C NMR spectra were taken on a GE NT-300 wide bore multinuclear NMR spectrometer at ambient temperature (generally 24° C). The ^{31}P NMR spectra were referenced to external 85% phosphoric acid, and the ^{13}C NMR spectra were referenced to internal tetramethylsilane. Chemical shifts that are

Table 1

^{31}P NMR data for the $Ph_2P(CH_2CH_2O)_2CH_3$ and Ph_2PMe complexes.

Compound	δ ^{13}P [a] (ppm)	$\lvert^1J(RhP)\rvert$ (Hz)	$\lvert^2J(PP)\rvert$ (Hz)
(cod)Rh{$Ph_2P(CH_2CH_2O)_2CH_3$-*P*}Cl (II)	28.71 d	150.	
ClRh{$Ph_2P(CH_2CH_2O)_2CH_3$-*P*}$_3$ (III)	37.22 dt	186	39 [b]
	22.49 dd	138	39 [c]
[(cod)Rh{$Ph_2P(CH_2CH_2O)_2CH_3$-*P,O*}]BF_4 (IV)	30.63 d	149	
[(cod)Rh{$Ph_2P(CH_2CH_2O)_2CH_2$-*P*}$_2$]BF_4 (V)	17.60 d	144	
[(coe)(Ph_2PMe)Rh(μ-Cl)]$_2$ (VI)	40.41 d	187	
[(Ph_2PMe)$_2$Rh(μ-Cl)]$_2$ (VII)	33.98 d	196	
ClRh(Ph_2PMe)$_3$ (VIII)	32.69 dt	186	41 [b]
	17.38 dd	140.	42 [c]
[{$Ph_2P(CH_2CH_2O)_2CH_3$-*P,O*}Rh(μ-Cl)]$_2$ (IX)	51.28 d	189	
[(coe){$Ph_2P(CH_2CH_2O)_2CH_3$-*P*}Rh(μ-Cl)]$_2$ (X)	39.08 d	195	
[{$Ph_2P(CH_2CH_2O)_2CH_3$-*P*}$_2$Rh(μ-Cl)]$_2$ (XI)	38.79 d	197	
trans-Cl(CO)Rh{$Ph_2P(CH_2CH_2O)_2CH_3$-*P*}$_2$ (XII)	22.28 d	124	

[a] d = doublet, dd = doublet of doublets, dt = doublet of triplets. [b] P *trans* to Cl. [c] P *trans* to P.

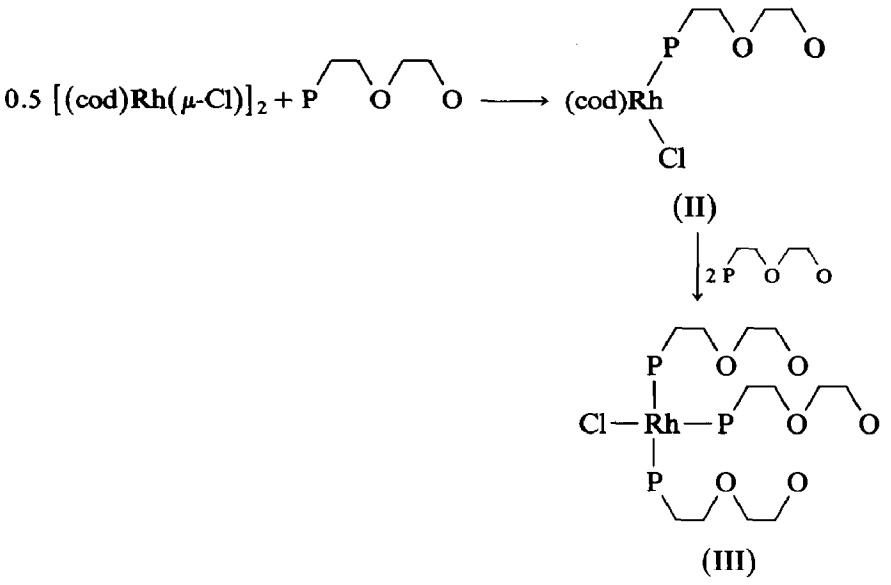
downfield from those of the reference compounds are reported as positive. The ^{31}P NMR data for the complexes are given in Table 1.

Preparation of reaction mixtures for the NMR studies

All NMR samples were prepared in a nitrogen-filled glove box. The Rh precursor was suspended in the NMR solvent, and the mixture was stirred as the phosphine ligand was added from a pipette. After the addition, the reaction mixture was stirred until it became homogeneous, and then it was transferred into an NMR tube. The NMR tube was capped, and the cap was sealed with parafilm before the tube was removed from the glove box to insure that an inert atmosphere was maintained. The reaction with silver tetrafluoroborate was carried out in a similar manner except that the reaction was run in the dark, and the mixture was filtered through Celite to remove the silver chloride precipitate before the NMR spectra were taken. Each reaction mixture was allowed to stand for several hours before the NMR spectra were obtained to ensure that the spectra were taken of equilibrium mixtures.

Results and discussion

The study of the reactions of [(cod)Rh(μ-Cl)]$_2$ or [(coe)$_2$Rh(μ-Cl)]$_2$ (cod = 1,5-cyclooctadiene, coe = *cis*-cyclooctene) with phosphines is complicated by the fact that both the starting materials and products are unstable. It is often not possible to obtain the products in analytical purity or to grow X-ray quality crystals. The best



Scheme 1. Reactions of $[(cod)Rh(\mu\text{-}Cl)]_2$ with I.

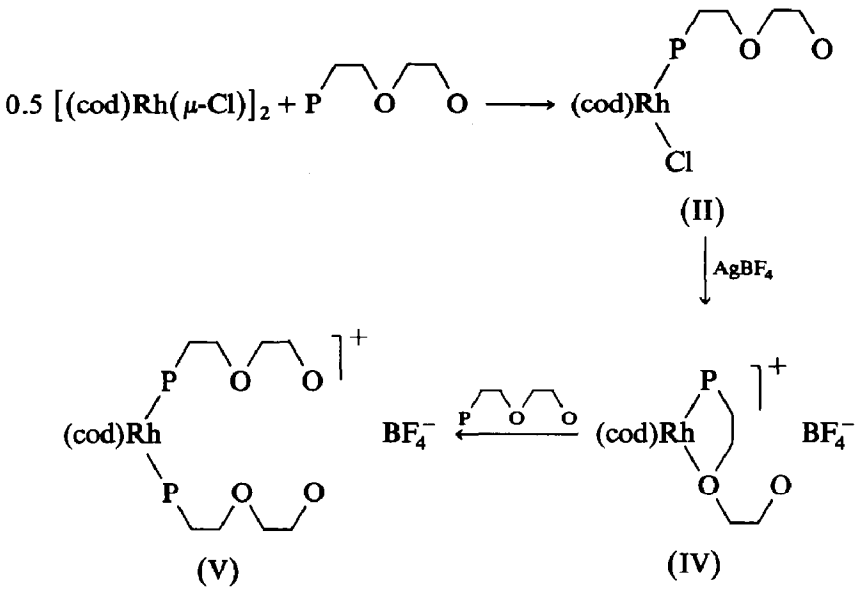
method for studying these reactions has proven to be ^{31}P NMR spectroscopy because the chemical shifts and one bond Rh–P coupling constants of the resonances are very sensitive to the nature of the groups coordinated to the Rh.

All of the Rh complexes of $Ph_2P(CH_2CHO)_2CH_3$ (I) slowly decompose in acetone-d_6 solution to form a complex containing oxidized I as a ligand (^{31}P NMR: δ 27.34 ppm, s). The ^{31}P NMR spectrum of this complex is similar to those reported for other phosphine oxide complexes of Rh [17,18]. When this material is treated with diethyl ether, an insoluble orange solid and the free oxide of I (^{31}P NMR: δ 29.79 ppm, s) are formed.

Reactions of [(cod)Rh(μ-Cl)]$_2$ with I

The reactions of I with $[(cod)Rh(\mu\text{-}Cl)]_2$ are summarized in Scheme 1. With a Rh/I ratio of 1/1, a single P-containing product (II) is obtained (^{31}P NMR: δ 28.71 ppm, d, $|^1J(RhP)|$ 150 Hz). The ^{31}P NMR spectrum of II is nearly identical to that reported for $(cod)Rh(Ph_2PCH_2C_4H_7O\text{-}P)Cl$ (C_4H_7O = 2-tetrahydrofurfuryl) (^{31}P NMR: δ 28.5 ppm, d, $|^1J(RhP)|$ 150 Hz) [5]. The *ipso, ortho* and *meta* phenyl resonances in ^{13}C NMR spectrum of II are doublets (^{13}C NMR: *ipso* δ 134.68 ppm, d, $|^1J(PC)|$ 72 Hz; *ortho* δ 134.58 ppm, d, $|^2J(PC)|$ 16 Hz; *meta* δ 128.67 ppm, d, $|^3J(PC)|$ 15 Hz) which indicates that only one P is coordinated to each Rh. These data suggest that II is $(cod)Rh\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P\}Cl$. Addition of a second equivalent of I to the acetone-d_6 solution of II causes the ^{31}P NMR resonance of II to broaden and decrease in intensity and ^{31}P NMR resonances of the tris complex $ClRh\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P\}_3$ (III) to appear. No ^{31}P NMR resonances that can be assigned as due to $[(cod)Rh\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P\}_2]Cl$ are observed. When a third equivalent of I is added to this solution, only resonances for III are observed in the ^{31}P NMR spectrum of the reaction mixture.

The preceding assignment for II is not consistent with those made by Anderson and Kumar for the products of the reactions of $[(cod)Rh(\mu\text{-}Cl)]_2$ with phosphines



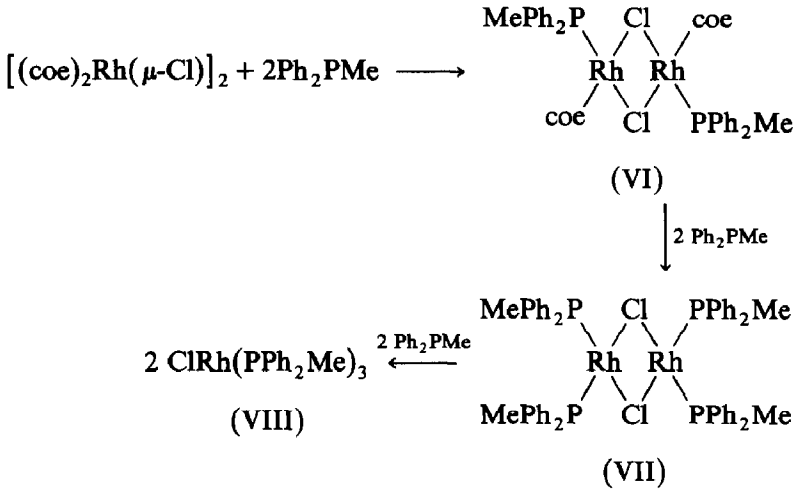
Scheme 2. Reactions of $[(cod)Rh(\mu\text{-}Cl)]_2$ with I.

(Ph_3P and $Ph_2PCH_2CH_2OCH_3$) when the Rh/phosphine ratios were 1/1 or 1/2 [3]. These authors suggest that the products of these reactions are complexes of the type [(cod)Rh(phosphine)$_2$]Cl. In order to prove that the assignment made for II is correct, the reactions shown in Scheme 2 have been carried out. Compound II, in acetone-d_6 solution, reacts with silver tetrafluoroborate to form a single new complex, IV, (^{31}P NMR: δ 30.63 ppm, d, $|^1J(RhP)|$ 149 Hz). The *ipso, ortho* and *meta* phenyl ^{13}C NMR resonances of IV are again doublets (^{13}C NMR: *ipso* δ 131.45 ppm, d, $|^1J(PC)|$ 69 Hz; *ortho* δ 134.19 ppm, d, $|^2J(PC)|$ 17 Hz; *meta* δ 129.46 ppm, d, $|^3J(PC)|$ 16 Hz), but they have quite different chemical shifts than do those of II. On the basis of this information and of the similarity of the ^{31}P NMR spectrum of IV to that of [(cod)Rh($Ph_2PCH_2C_4H_7O$-*P,O*)]SbF_6 (C_4H_7O = 2-tetrahydrofurfuryl) (^{31}P NMR: δ 38.6 ppm, d, $|^1J(RhP)|$ 151 Hz) [5], the most probable assignment for IV is [(cod)Rh{$Ph_2P(CH_2CH_2O)_2CH_3$-*P,O*}]BF_4. Compound IV reacts with a second equivalent of I in acetone-d_6 solution to form [(cod)Rh{$Ph_2P(CH_2CH_2O)_2CH_3$-*P*}$_2$]BF_4 (V). The ^{31}P NMR spectrum of this complex is very similar to that of [(cod)Rh{$Ph_2P(CH_2CH_2O)_2CH_3$-*P*}$_2$](ClO_4) (^{31}P NMR (chloroform-d_1): δ 16.09 ppm, d, $|^1J(RhP)|$ 143 Hz) which has previously been prepared in analytical purity by the reaction of I and (cod)Rh(acac) in the presence of perchloric acid [14].

The ^{31}P NMR data reported by Anderson and Kumar for the products of the reactions of $[(cod)Rh(\mu\text{-}Cl)]_2$ with phosphines (phosphine = $Ph_2PCH_2CH_2OCH_3$, ^{31}P NMR (acetone): δ 25.6 ppm, d, $|^1J(RhP)|$ 149 Hz; phosphine = PPh_3 (acetonitrile), ^{31}P NMR: δ 27.1 ppm, d, $|^1J(RhP)|$ 147 Hz) are very similar to those for II. This suggests that the reaction products assigned by Anderson and Kumar as cationic [(cod)RhL_2]Cl complexes may instead be neutral (cod)Rh(L)Cl complexes.

Reactions of $[(coe)_2Rh(\mu\text{-}Cl)]_2$ with Ph_2PMe

The reactions of Ph_2PMe with $[(coe)_2Rh(\mu\text{-}Cl)]_2$ are summarized in Scheme 3. If the Rh/Ph_2PMe ratio is 1/1, the product is [(coe)(Ph_2PMe)Rh(μ-Cl)]$_2$ (VI), and if



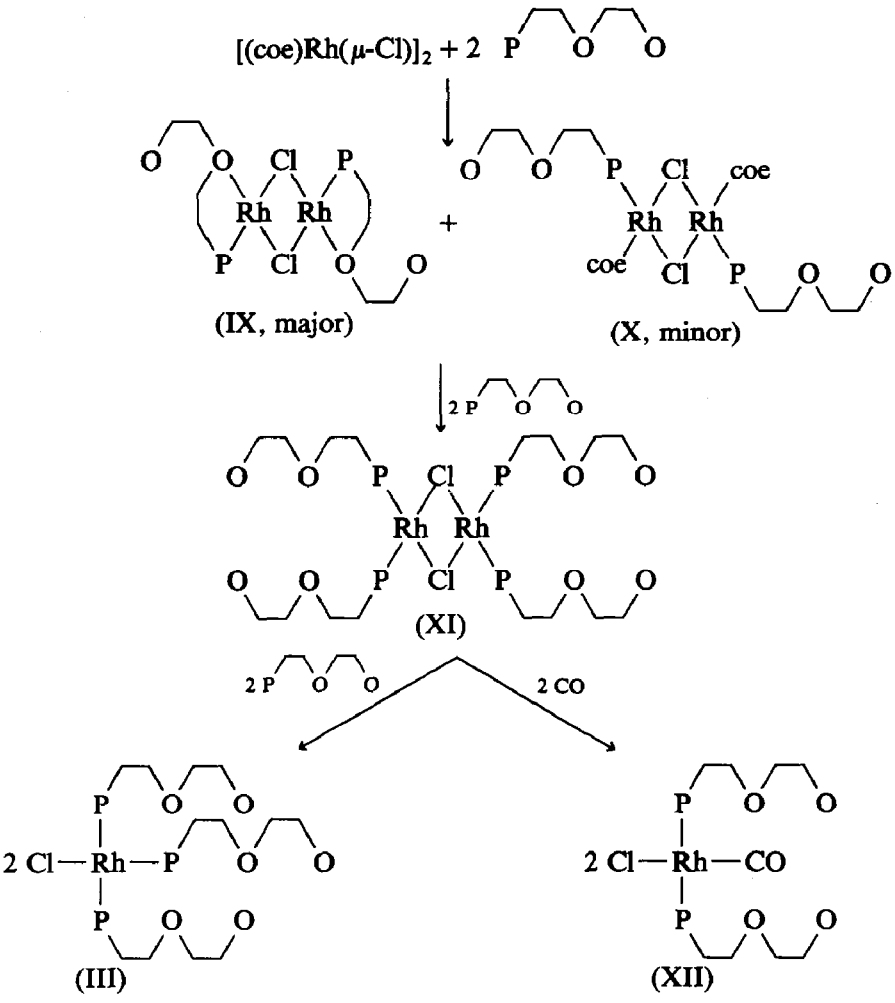
Scheme 3. Reactions of $[(coe)_2Rh(\mu\text{-}Cl)]_2$ with Ph_2PMe.

the Rh/Ph_2PMe ratio is 1/2 the product is $[(Ph_2PMe)_2Rh(\mu\text{-}Cl)]_2$ (VII). The ^{31}P NMR spectra of these products are similar to those reported for other chloro-bridged dimers of Rh that are obtained from the reactions of monodentate phosphines with $[(coe)_2Rh(\mu\text{-}Cl)]_2$ [19,20]. In particular, the ^{31}P NMR resonances of the complexes exhibit the large $|^1J(RhP)|$ values expected for Rh–P groups *trans* to a weak donor atom such as chloride [13,21]. With a Rh/Ph_2PMe ratio of 1/3, the reaction product is the expected tris-substituted complex, $ClRh(Ph_2PMe)_3$ (VIII).

The reactions of monodentate phosphines with $[(cod)Rh(\mu\text{-}Cl)]_2$ and $[(coe)_2Rh(\mu\text{-}Cl)]_2$ at Rh/ligand ratios of 1/1 and 1/2 give quite different products. This appears to be due to the fact that the bidentate cod ligand is much more strongly bound to the Rh than is the monodentate coe ligand. Because of this, the first step in the reactions of monodentate phosphines with $[(cod)Rh(\mu\text{-}Cl)]_2$ involves cleavage of the chloride bridge, but the first step of the reactions of monodentate phosphines with $[(coe)_2Rh(\mu\text{-}Cl)]_2$ involves displacement of one of the coe ligands.

Reactions of $[(coe)_2Rh(\mu\text{-}Cl)]_2$ with I

The reactions of $[(coe)_2Rh(\mu\text{-}Cl)]_2$ with I are shown in Scheme 4. With a Rh/I ratio of 1/1, the reaction mixture contains primarily IX (^{31}P NMR: δ 51.28 ppm, d, $|^1J(RhP)|$ 189 Hz) with a small amount of X (^{31}P NMR: δ 39.08 ppm, d, $|^1J(RhP)|$ 195 Hz). Complex IX is assigned as $[\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P,O\}Rh(\mu\text{-}Cl)]_2$ because chelation of I to form a five-membered ring should result in the observed downfield shift in the ^{31}P NMR resonance [22]. The minor component (X) is assigned as $[(coe)\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P\}Rh(\mu\text{-}Cl)]_2$ on the basis of the similarities of its ^{31}P NMR spectrum with that of the analogous Ph_2PMe complex (VI). The fact that IX, with I as a bidentate, chelating ligand, is the major product rather than X, as would be expected based upon the analogous reaction with Ph_2PMe, is consistent with the weak coordination of the coe to the Rh discussed previously. A complex similar to IX would not be expected to be formed from the reaction of $[(cod)Rh(\mu\text{-}Cl)]_2$ and I at a 1/1 Rh/I ratio because this would require the displacement of the strongly coordinating cod from the Rh by the weakly coordinating ether.



Scheme 4. Reactions of $[(coe)_2Rh(\mu\text{-}Cl)]_2$ with I.

The addition of I to the 1 : 1 reaction mixture causes the ^{31}P NMR resonances of IX and X to decrease and that of a new compound, XI (^3P: δ 38.79 ppm, d, $|^1J(RhP)|$ 197 Hz) to appear. When the Rh/I ratio reaches 1/2, only the ^{31}P NMR resonance for XI is observed in the ^{31}P NMR spectrum of the reaction mixture. Complex XI is assigned as $[\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P\}_2Rh(\mu\text{-}Cl)]_2$ because the chemical shift and $|^1J(RhP)|$ of its ^{31}P NMR resonance are very similar to those of X and of VII. This assignment is further supported by reaction of XI with CO to yield the expected product, *trans*-$Cl(CO)Rh\{Ph_2P(CH_2CH_2O)_2CH_3\text{-}P\}_2$ (XII). The chemical shift and $|^1J(RhP)|$ of the ^{31}P NMR resonance of XII are very similar to those reported for other *trans*-Cl(CO)Rh(phosphine)$_2$ complexes [19,20,23,24]. The presence of a single CO ligand in XII is indicated by a single, strong absorption at 2010 cm^{-1} in the IR spectrum of XII.

The fact that the ether group rather than the bridging chloride is displaced by the phosphine in the reaction of IX with I indicates that the ether is very weakly coordinated to the Rh. This is consistent with earlier studies of the coordination

chemistry of I in which I was observed to coordinate to a variety of different metal centers solely through the diphenylphosphino group [14].

The addition of I to the 1/2 reaction mixture causes the ^{31}P NMR resonance of XI to decrease and those of $ClRh\{Ph_2P(CH_2CH_2O)_2CH_3\}_3$ (III) to appear. When the Rh/I ratio reaches 1/3, only III is observed in the reaction mixture.

Conclusions

Because the reaction products of I with $[(cod)Rh(\mu\text{-}Cl)]_2$ and $[(coe)_2Rh(\mu\text{-}Cl)]_2$ cannot be isolated in analytical purity and cannot be crystallized to obtain X-ray quality crystals, the natures of these products have been determined using ^{31}P and ^{13}C NMR spectroscopy. These studies have shown that excess I reacts with both $[(cod)Rh(\mu\text{-}Cl)]_2$ and $[(coe)_2Rh(\mu\text{-}Cl)]_2$ to give $ClRh\{Ph_2P(CH_2CH_2O)_2CH_3\}_3$ as expected. However, at Rh/I ratios of 1/1 and 1/2, the two Rh complexes give quite different products due to the different coordinating abilities of the monodenate coe and bidentate cod ligands. The reactions of I with $[(coe)_2Rh(\mu\text{-}Cl)]_2$ or with $[(cod)Rh(\mu\text{-}Cl)]_2$ and $AgBF_4$ at Rh/I ratios of 1/1 give complexes containing I as a P,O-chelating ligand. These are the first examples of I serving as a chelating ligand.

Acknowledgements

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